Sewage sludge based carbons for catalytic wet air oxidation of phenolic compounds in batch and trickle bed reactors

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ABSTRACT

The potential of using sludge based activated carbons (SBACs) for catalysing the wet air oxidation (WAO) of phenol, o-cresol, o-chlorophenol and p-nitrophenol was assessed in both a batch slurry reactor and a continuous trickle-bed reactor. In the batch reactor, the activity of two powdered carbons prepared from, respectively, dewatered raw (DRAW) sludge and dewatered, mesophilic anaerobically digested (DMAD) sludge was tested at 160 °C and 4.2 bar of oxygen partial pressure. Continuous, trickle-bed reactor experiments of up to 72 h were conducted at similar operating conditions to study the durability and catalytic wet air oxidation (CWAO) performance of three economically promising steam activated SBACs. Due to their low mechanical strength, the two DRAW derived SBACs tested were produced using two different attrition resistance enhancement techniques. A commercial activated carbon (Chemviron, AP4-X) was employed as the reference catalyst for all of the tests.

In the batch runs, the SBACs and AP4-X achieved high levels of pollutant conversion in the case of phenol, o-cresol and o-chlorophenol. However, irrespective of the carbon tested, p-nitrophenol was resistant to oxidation. When employed in the trickle-bed reactor, the DRAW derived SBAC pelletised using a lignosulphonate binder was found to be the most stable carbon. With this carbon the order of compound reactivity was as observed in the batch experiments.

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1. Introduction

Wet oxidation (WO) is an established and industrially applied process for the oxidation of organic and inorganic substances in an aqueous solution or suspension by means of oxygen or air at elevated temperatures [1]. In order to destroy biotoxic and/or refractory organic compounds by wet air oxidation (WAO), temperatures and air pressures in the range of 200–300 °C and 30–70 bar, respectively, are required. However, research conducted over the past 20 years has shown that these high and economically punitive pressures and temperatures can be reduced through the use of noble metal or metal oxide supported catalysts [2–4]. On the other hand, these catalysts are considered to be too expensive for their large-scale utilisation in industrial WAO applications. Hence, cheaper catalysts have to be developed in order to improve the process economics [4].

Recently, certain commercial and modified activated carbons have been found to exhibit sufficient catalytic activity to promote the liquid phase oxidation of phenolic pollutants [2,5–9]. In this context, two exploratory studies carried out by this research consortium investigated the preparation and use of sewage sludge based activated carbons (SBACs) to effect the catalytic wet air oxidation (CWAO) of phenol in, respectively, a batch reactor [10] and a hybrid adsorption-oxidation process [11]. For the batch reactor tests, two different sludges were used in the preparation of the carbons: dewatered raw filter cake (DRAW) and dewatered, mesophilic anaerobically digested sludge (DMAD): the production of activated carbons from these sludges was first described by Pullket et al. [12]. It was found that despite their relatively low surface areas, which stemmed from their high ash content, the SBACs exhibited high levels of phenol conversion. The SBACs' catalytic properties appeared to result from their high content of surface functional groups and moreover, their high Fe content [10,11].

The strong interest in using SBACs arises from their environmental sustainability and their potentially low cost (in comparison to conventional activated carbons); for further information, consultation of the review paper by Smith et al. [13] is advised. A preliminary study on the CWAO of phenol using SBACs in a trickle-bed reactor has provided some preliminary results [14]. However, to further confirm that the SBACs are commercially viable, it is necessary

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to verify that they can promote the remediation of phenolic compounds in a CWAO reactor. Hence, in the first part of this follow-up study, the batch oxidation of phenol, o-cresol, o-chlorophenol and p-nitrophenol was investigated using two SBACs prepared from each sludge feedstock (DMAD and DRAW). In the second part, the performance of three economically promising steam activated SBACs was assessed in experiments of up to 72 h in duration within a trickle-bed reactor. The performance of the SBACs was compared with the commercial Chemviron carbon AP4-X, which had been specifically recommended for use in CWAO wastewater treatment processes.

Of the two sludge types tested, the DRAW sludge had previously been shown to yield the SBACs with the highest levels of phenol and TOC removal in the batch CWAO of phenol [10]. However, these SBACs were also found to exhibit an unacceptably low attrition resistance [10,11,14]. A key objective of this study was therefore to appraise two different techniques for producing DRAW derived SBACs with an enhanced attrition resistance.

2. Experimental

2.1. Materials

The aqueous solutions subjected to CWAO were prepared with deionised water and respectively, analytical grade phenol, o-cresol, o-chlorophenol and p-nitrophenol. A uniform concentration of 5 g/l was employed, except for o-chlorophenol, for which a concentration of 1 g/l was utilised. Tbis was necessary to minimise the corrosion caused by the chloride ions liberated during its oxidation. The gaseous oxidant fed to the reactor was compressed high purity synthetic air.

A granular commercial activated carbon (AP4-X) supplied by Chemviron Carbons Ltd. in the form of 2.5 mm pellets served as a reference catalyst. Prior to use in the batch or continuous experiments, all carbons were crushed and sieved to obtain particles smaller than 0.2 mm or in the range of 0.3–0.7 mm, respectively

2.1.1. Preparation of SBACs

The SBACs were prepared from two municipal sewage sludge samples: DRAW, sourced from Little Marlow WWTP (UK) and DMAD, which was obtained from Ashford WWTP (UK). After collection, the sewage sludges were sterilized at 121 °C for 15 min (Priorclave Direct Steam Autoclave, London, UK) and then dried at 105–110 °C to constant mass. They were crushed to below 10 mm using a cross beater mill (Glen Creston, London, UK) and stored in air tight containers prior to further use.

The steam activated SBACs were produced using a Carbolite 11/150 laboratory scale rotary furnace (Carbolite, Hope Valley, UK) as described in Marques et al. [10]. The preparation conditions and respective labels of the SBACs used in this study are listed in Table 1. Further specific conditions employed in the preparation of the SBACs are given below.

2.1.1.1. Post-activation thermal treatment. One steam activated DRAW carbon (DR-SA-C950) was heated at a rate of 10 °C/min to 950 °C under a nitrogen flow of 500 ml/min and then held at this temperature for 0.5 h. After carbonisation, the nitrogen flow was stopped and the furnace was automatically cooled to room temperature.

2.1.1.2. Chemical activation. The chemically activated SBAC was produced by physically mixing DMAD sludge with K_2CO_3 at a ratio of 1:1 (dry by mass). A mass of 30 g of this mixture was then dried at 105 °C overnight before being loaded into an Alsint tube reactor (Multi-lab, Newcastle, UK). The reactor was purged with nitrogen at a flow rate of 500 ml/min and heated at a rate of 18–20 °C/min

Table 1
Labels of SBACs tested in CWAO of phenol and the conditions employed in their preparation.

Label	Preparation method of carbon
DM-SA	DMAD activated with steam at 838 °C for 73 min (heating rate of 10 °C/min)
DM-K-W	DMAD activated with K_2CO_3 (1:1 by dry mass), further washed with distilled water, boiled for 1 h
DR-SA	DRAW activated with steam at 900 °C for 100 min (heating rate of 10 °C/min)
DR-SA-C950	DRAW activated with steam at 900 °C for 100 min (heating rate of 10 °C/min), carbonised at 950 °C for 0.5 h
DR-SA-PV	DRAW-SA (steam activated at 838 °C for 80 min) and pelletised with 5% of PVA binder
DR-SA-LS	Carbonised DRAW (700 °C, 1 h) pelletised with 10% of LSA binder then steam activated at 838 °C for 80 min
AP4-X	Commercial carbon provided by CHEMVIRON

in a horizontal tube furnace (Carbolite, Hope Valley, UK) at 800 °C for 60 min. After the furnace had cooled to room temperature, the sample was recovered and subsequently, it was heated in reverse osmosis (RO) water for 1 h to leach out the activation by-products; the liquid to solid ratio employed was 10 ml/g. The solids were subsequently recovered by filtration through Whatman No. 1 paper (particle retention size of 11 μm) and washed with RO water until a stable pH was obtained in the filtrate.

2.1.1.3. Enhancement of the SBACs' attrition resistance for tricklebed oxidation. Two techniques were employed to enhance the hardness of the DRAW derived SBACs; prior to treatment the SBACs were mechanically milled below ca. 100 μm. For DR-SA-PV, the milled SBAC (steam activated at 838 °C for 80 min) was mixed with water and a 5 wt.% loading of an organic binder (poly vinyl alcohol, Nippon Gohsei, Kingston upon Hull, UK) and then hand extruded to form pellets, which were subsequently dried (105–110 °C) and crushed into particles of 0.5–2 mm in size. For DR-SA-LS, the milled SBAC (DRAW sludge carbonised at 700 °C for 1 h) was mixed with water and a 10 wt.% loading of a lignosulphonate based binder: Borresperse AM320 (Borregaard UK Ltd., Warrington, Cheshire, UK). Pellets were formed by uniaxial, compression and after drying, they were steam activated for 80 min at 838 °C.

2.2. Characterisation of carbons

For characterisation the SBACs and AP4-X carbon were crushed and sieved to a particle size below 150 μm. Their surface area and porosity was determined using a Coulter Omnisorp® 100 (Beckman-Coulter, UK) following the protocol reported in Marques et al. [10] and Pullket et al. [12]. The ash content of the carbons was measured using the method prescribed by ASTM standard D 2866-94 [15].

The FTIR spectra were obtained using a MAGNA 560 IR Spectrometer (Nicolet, USA). The number of scans and the scanning resolution were set to 250 and 4 cm^{-1} respectively. Before analysis, a background measurement was made of the air within the sample chamber to correct the subsequent sample spectrum using the FTIR software. Prior to analysis it was necessary to mount the samples in a KBr medium. Thus, samples were dried, mixed with KBr (Spectrosol grade, VWR International Ltd., Poole, UK) at a ratio of ca. 1:150 (w/w) and crushed using an agate pestle and mortar. Due to its high carbon content and hence high absorbance of IR radiation, it was necessary to use a ratio of 1:250 for AP4-X. Approximately 150 mg of the sample-KBR mixture was loaded into a pneumatic, 13 mm die press (Specac, UK) and a disk was formed by applying 10 metric tonnes of pressure for a period of 10 min.

The inorganic elemental content of the SBACs was measured using a Perkin Elmer Optima 7300 DV Optical Emission Spectrometer (UK). Prior to analysis, their organic content was eliminated by heating the samples in air at 650 °C in a muffle furnace overnight. The samples were then digested in accordance with a standard aqua regia method [16], although in order to take account of the operating limits of the microwave digester (Anton Paar Multiwave 3000, UK) the heating program was adapted from an EPA, microwave digestion method [17]: ramp to 170 °C in 10 min, hold at 170 °C for 20 min. The sample weight employed was 0.100 g (±0.001 g).

The pH of the carbons was determined using a method derived from Bagreev et al. [18]. After being dried for 3 h at 150 °C, 0.4 g of the sample was added to 20 ml of deionised water. The mixture was mechanically agitated for 24 h and after the removal of the carbon by filtration with No. 1 filter paper, the pH of the recovered solution was measured using a calibrated pH probe & meter (Hydrus 500, Fisher Scientific, UK).

2.3. Catalytic tests in batch and trickle bed reactors

2.3.1. Batch reactor

The oxidation of phenol, o-cresol, o-chlorophenol and p-nitrophenol over the SBACs and commercial carbon was assessed in batch experiments conducted for 4 h at 160 °C and 4.2 bar of oxygen partial pressure. In a standard experiment, 100 ml of pollutant solution and 2 g of carbon were mixed in the high pressure autoclave. Then, the reactor vessel was closed, leak proofed at 25 bar (room temperature) and placed in a furnace to heat the phenol–carbon slurry to 160 °C under a minimal stirrer speed. Prior to initiating the reaction, phenol adsorption was allowed to occur and a 2–3 ml specimen of the liquid was taken after *ca.* 25 and 50 min. Subsequently, the reaction was started by increasing the stirrer speed up to 1000 rpm and liquid samples were taken after 30, 60, 120 and 240 min to measure compound and TOC removal. Further experimental details can be found in Marques et al. [10].

2.3.2. Trickle bed reactor

The reactor (stainless steel, ID = 1 cm, *L* = 20 cm) used for the continuous oxidation experiments was filled with 7–7.5 g of carbon and placed in an electrical oven for heating and temperature control: a schematic of the trickle bed reactor (TBR) rig is illustrated in Fig. 1. Prior to initiating each experiment, the reactor was leak checked at room temperature with air at 25 bar or 50 bar. If no leaks were detected, the operating pressure was adjusted with the help of a pressure reducing valve and the pollutant solution was fed from a 5 l feed tank to the reactor by a high-pressure pump. The liquid flow rate was measured with a liquid mass flow meter installed after the liquid dampers in the exit line of the pump. The liquid and air streams were mixed downstream and preheated to the desired reaction temperature in a 1 m long coil placed inside the oven. The exit solution from the reactor was directed to sampling and G-L separation devices. The liquid was stocked in the G-L separator and the exit gas was vented through a needle valve to a gas flow meter to measure the gas flow rate.

The catalytic activity and stability of the carbons were assessed through 72 h experiments at fixed liquid and gas flow rates of 60 ml/h and 9 l/h (STP) respectively. The operating temperatures and oxygen partial pressures ranged from 120 to 160 °C and 2 to 8 bar, respectively. During the experiments, 5 ml liquid specimens were taken at regular time intervals to measure both the degree of compound and TOC removal and the concentration of metal ions leached from the carbons (see Section 2.4).

2.4. Analytical methods

Phenolic compound concentrations of liquid samples were all determined by HPLC (model 1100 Agilent Technologies). The analysis was performed with a C18 reverse phase column (Hypersil ODS, Agilent Technologies). The mobile phase of HPLC grade methanol (Aldrich) and ultra-pure-water (Millipore Direct-Q system) was maintained at a ratio of 40:60 (v/v) and fed into the column at a flow rate of 1 ml/min. The wavelength in the diode array detector was set to 254 nm. The total run time of this analytical procedure was 6 min, except for some long term (30 min) analyses of liquid samples withdrawn during experiments using the DM-SA carbon. This short procedure allowed for the detection and quantification of the phenolic compound peaks. Detection of the intermediates was beyond the scope of this work. However, the HPLC analysis conducted in the batch oxidation of phenol over SBACs [10] essentially corroborated the classical phenol destruction routes of Devlin and Harris [19].

For total organic carbon (TOC) measurement, a TOC analyzer equipped with a non-dispersive infrared detector (NDIR) was employed. Prior to analysis, the liquid samples were acidified to a pH of 2 with 2 N HCl to completely dissolve any inorganic carbon that may have been present. The respective degrees of compound and TOC conversion were calculated from the raw experimental data according to:

$$X = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \tag{1}$$

where C_{in} and C_{out} are the inlet and outlet concentrations of compound and TOC, respectively.

In order to determine the degree of metal leaching from the carbon matrix, the solutions recovered from the CWAO experiments were filtered to obtain a clear liquid. Detection and quantification of metals were then conducted on a fraction of this liquid by means of atomic absorption spectroscopy. The instrument was calibrated using prepared standard solutions with known concentrations of Fe, Cu, Cr, Mn, Mg and Ca.

At the end of each CWAO test in the TBR, the spent carbon was dried in the reactor at 105 °C for 12 h to remove the excess water, carefully recovered from the reactor and weighed to determine the carbon burn-off. For each spent DM-SA carbon, a small fraction of *ca.* 25 mg was prepared for thermogravimetric analysis (TGA). The analysis was carried out in a Thermobalance (Perkin-Elmer, TGA7-TCA7) that measured the weight change of the sample during heating from 100 °C to 900 °C at a rate of 10 °C/min under constant nitrogen flow.

3. Results and discussion

3.1. Characterisation of SBACs and AP4-X carbon

The textural characteristics of the SBACs and the reference commercial carbon (AP4-X) used in this work are displayed in Table 2. It is evident that the BET surface area of AP4-X is greatly in excess of the surface areas of the SBACs, which as previously reported [10], is consistent with its considerably lower ash content and ergo, higher content of microporous carbon. The SBACs possess BET surface areas of the same order (179–269 m²/g), except for DM-K-W (422 m²/g). The hardened SBAC produced using the lignosulphonate binder, DR-SA-LS, exhibits the highest surface area of the SBACs prepared without chemical activation. Moreover, it possesses a micropore surface area that is five times greater than its mesopore and macropore surface area; the other SBACs exhibit micropore surface areas that are lower than their meso- and macro-pore surface areas. This outcome can be attributed to the lignosulphonate binder: previous research has shown that lignin can
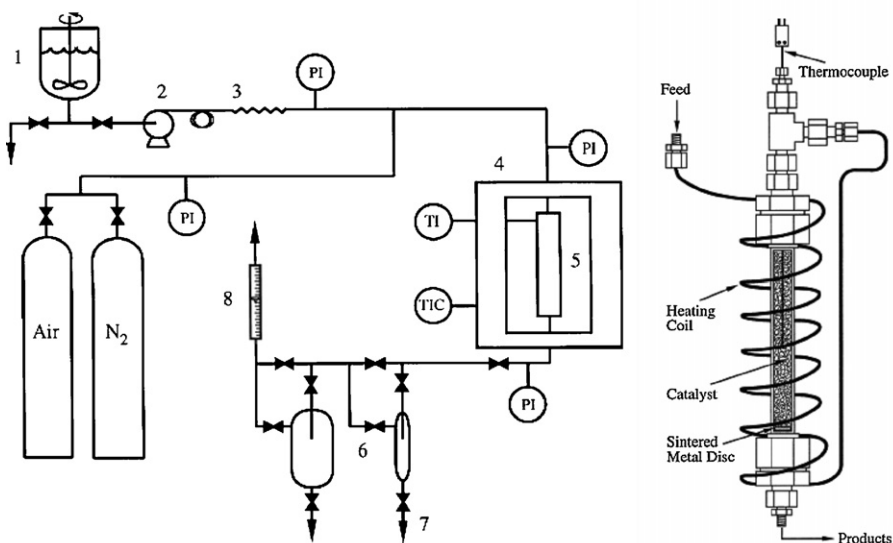
Fig. 1. Experimental set-up for continuous CWAO of phenol: (1) feed vessel, (2) high pressure liquid pump, (3) pulse dampener, (4) oven, (5) trickle bed reactor, (6) gas liquid separator, (7) sampling and (8) gas flow meter.

Table 2
Textural properties and Fe content of carbons studied.

SBAC	Ash (wt.%)	S_{BET} (m^2/g)	$S_{MesoMacro}$ (m^2/g)	S_{Micro} (m^2/g)	pH	Fe (µg/g)
DM-SA	78.2	179.3	107.7	71.6	7.6	106,069
DM-K-W	66.6	421.8	273.9	147.9	8.2	n.a.
DR-SA	77.4	214.4	139.0	75.4	10.1	106,605
DR-SA-C950	70.3	269.1	181.1	87.8	n.a.	n.a.
DR-SA-PV	63.4	197.2	146.5	52.5	7.9	87,322
DR-SA-LS	53.8	244.1	40.2	203.9	8.1	72,992
AP4-X	11.0	1013.4	161.2	852.2	7.8	11,584

readily be used as a feedstock for activated carbon production [20]. Thus, it can be concluded that the lignin back-bone of the binder has developed porosity through its activation and moreover, this porosity is primarily microporous in nature.

Lignosulphonate binders cure at high temperatures, which prompted the pelletisation of DR-SA-LS prior to its activation. The polyvinyl alcohol binder used to produce DR-SA-PV decomposed at high temperatures; hence it was added subsequent to the activation step. Consequently, the resulting SBAC exhibits an inferior surface area due to the binder's partial obstruction of the pores.

The results of the elemental analysis, in particular the Fe content, of the SBACs and AP4-X are also shown in Table 2. All of the SBACs exhibit high Fe concentrations (>72,000 µg/g) and AP4-X also exhibits an appreciable Fe content: 11,584 µg/g. The FTIR spectra of a selection of the SBACs are displayed in Fig. 2; the prominent peak centred at 3440–3450 cm^{-1} is associated with the presence of water (hydroxyl groups) and thus is disregarded from the subsequent discussion. The FT-IR spectra of DM-SA, DR-SA and APX-4 have been discussed previously and for more details the reader should consult Ref. [10].

Comparing the FT-IR spectra of DM-SA and DR-SA with the hardened DR-SA-LS and DR-SA-PV, there is a clear reduction in the intensity of the 1045–1084 cm^{-1} band, which is consistent with its lower inorganic content. Otherwise, the DR-SA-LS spectrum essentially exhibits the same profile as the DR-SA and DM-SA spectra. However, DR-SA-PV exhibits a new, albeit small band centred at 1715–1730 cm^{-1}. This is indicative of the carbonyl/acetate groups present in the cross-linked PVA resin [21,22]. The presence of cross-links is evidenced by both the high cohesive strength of the pellets and their water resistance.

3.2. Oxidation of phenolic compounds in the batch reactor

Among the available DRAW and DMAD based SBACs [10], the DR-SA-C950 and DM-K-W carbons were representatively selected as CWAO catalysts for the batch tests. The compound conversion time profiles obtained are plotted in Fig. 3; Table 3 lists the compound and TOC removals measured after 240 min of reaction. The results show that the SBACs and AP4-X yield high levels of compound (65–99%) and TOC (55–90%) removal for phenol, o-cresol
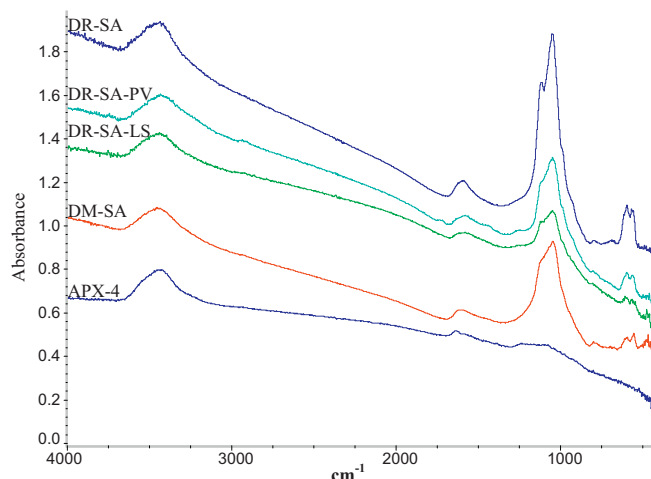

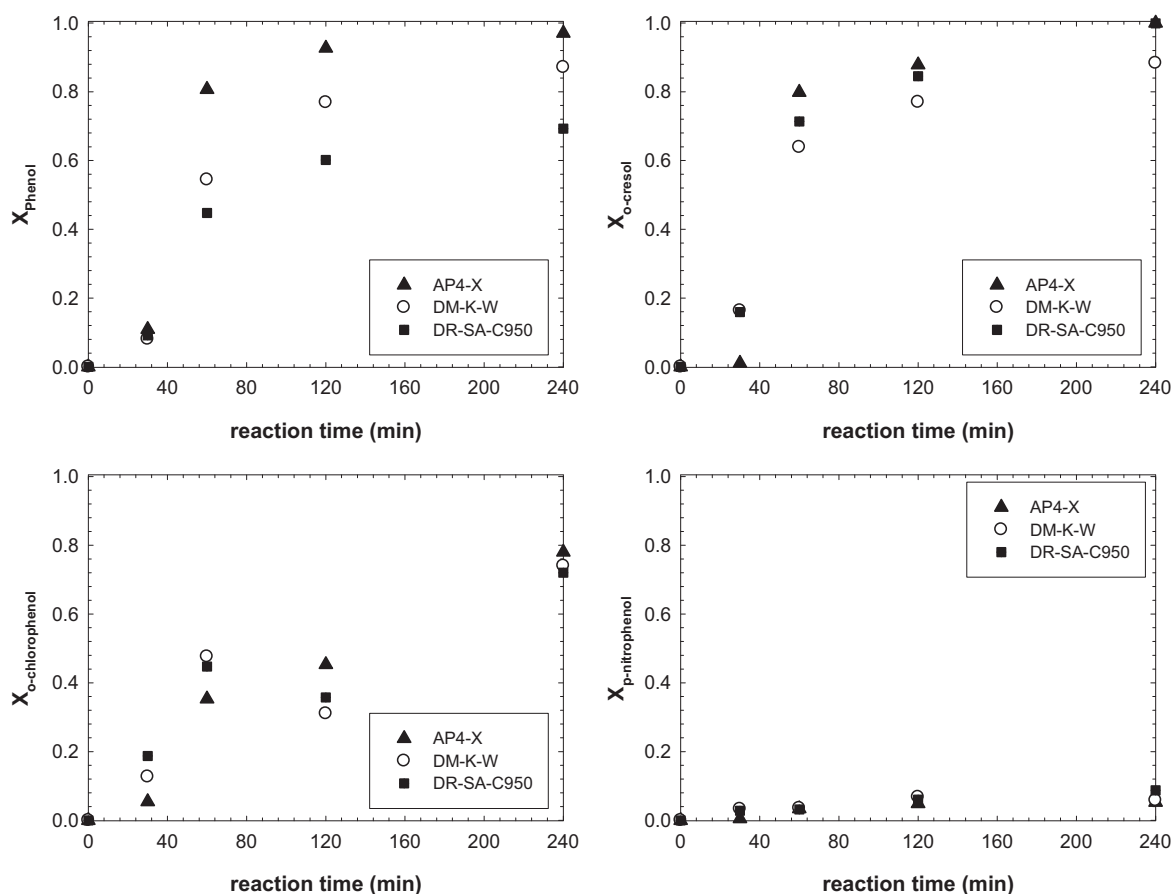**Fig. 2.** FT-IR spectra of AP4-X and selected specimens of the SBACs.

Fig. 3. Phenolic compound removal obtained in batch reactor for DR-SA-C950, DM-K-W and commercial AP4-X carbons: $T = 160\,^\circ\text{C}$, $P_{O_2} = 4.2$ bar, $W = 2$ g.

and o-chlorophenol. However, p-nitrophenol was found to be resistant to degradation during CWAO at $160\,^\circ\text{C}$ and 4.2 bar of oxygen partial pressure, irrespective of the carbon catalyst used. This outcome can be attributed to the p-nitrophenol molecule's NO_3 group, which has a strong deactivating effect. The following order of compound reactivity can thus be established: phenol > o-cresol > o-chlorophenol ≫ p-nitrophenol (except for DR-SA-C950, where the order is slightly different: o-cresol > o-chlorophenol ≈ phenol ≫ p-nitrophenol). This trend is in agreement with previous studies conducted on the CWAO of phenolic compounds over commercial ACs [2,5,6].

Due to its considerably higher surface area, the commercial AP4-X generally exhibits the best activity (as discussed in this paper's precursor study [10], all of the carbons exhibit appreciable quantities of Fe (>0.8 wt.%) and hence can be classed as being catalytically active; their surface area is therefore the primary determinant of their performance). Nevertheless, the differences in compound conversion performance are small for o-cresol and vanish in the case of o-chlorophenol. The chemically (K_2CO_3) activated DM-K-W carbon, which possesses the second highest surface area, outperforms the DR-SA-C950 carbon in the oxidation of phenol. However, the opposite trend has been observed for o-cresol.

Moreover, for this pollutant, DR-SA-C950 yielded the largest final TOC removal (87%) of all the carbons tested. This result reaffirms that the DRAW sludge is the better feedstock for the production of active SBACs, as highlighted in our previous study [10]. On the other hand, DR-SA-C950 also reveals the highest leaching of metal ions into the reaction solution, reflecting its inferior resistance to physical disintegration under the CWAO process. Finally, it must be mentioned that corrosive, free chloride ions are generated during o-chlorophenol oxidation. The enhanced corrosion of the stainless steel reactor material caused by these ions resulted in serious leak problems during operation.

3.3. Oxidation of phenol in the trickle-bed reactor

3.3.1. Catalytic performance of steam activated DM-SA carbon
3.3.1.1. Effect of sludge load on DM-SA activity. 72 h CWAO experiments conducted using two steam activated carbons prepared from different specimens of DMAD sludge (labelled load A and load B respectively), evidenced deviations in the order of 10–15% for phenol and TOC conversion [14]. The BET surface areas of the load A and load B derived SBACs are 138.7 and 125.5 m²/g, respectively. As shown in Table 2, the BET surface area of the DM-SA SBAC used for

Table 3
Oxidation of phenolic compounds in batch reactor: $T = 160\,^\circ\text{C}$, $P_{O_2} = 4.2$ bar, $W = 2$ g, $t = 240$ min.

SBAC	Phenol			o-Cresol			o-Chlorophenol			p-Nitrophenol		
	X_{Ph}	X_{TOC}	pH	X_{Ph}	X_{TOC}	pH	X_{Ph}	X_{TOC}	pH	X_{Ph}	X_{TOC}	pH
AP4-X	0.97	0.88	5.1	~1	0.81	4.5	0.85	0.61	2.5	0.05	–	6.2
DM-K-W	0.87	0.76	6.9	0.88	0.62	2.8	0.83	0.62	3.2	0.06	–	4.2
DR-SA-C950	0.65	0.55	5.1	~1	0.87	3.5	0.82	0.58	3	0.06	–	4.7

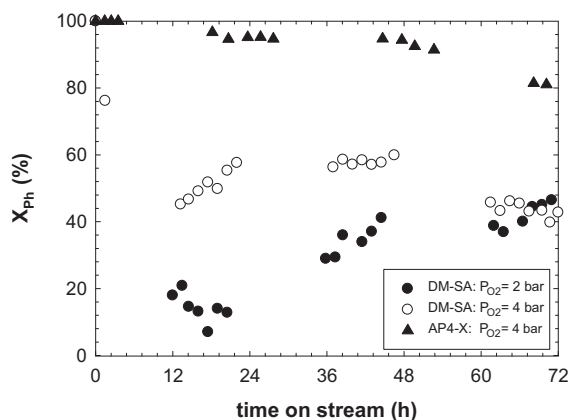**Fig. 4.** Phenol removal with time on stream for DM-SA and AP4-X carbons: $T = 160\,^\circ C$, $C_{Ph,0} = 5$ g/l, $\tau_L = 0.12$ h, $F_{air} = 9$ N l/h, $W = 7$ g.

the principal results displayed in this paper is $179\,m^2/g$, so clearly the heterogeneity of the sludge can result in noticeable differences in the surface area. However, all of these values are within the same order. Moreover, given their low size (relative to the surface area of the commercial carbon), such deviations cannot be viewed as being of great significance.

These results suggest that sludge heterogeneity does not lead to a significant variation in the catalytic activity of the SBACs. In fact, even in the case of commercial carbons, which are manufactured following a well defined preparation protocol, differences in phenol conversion of up to 10% have been observed in our laboratory. It is however recommended to occasionally check the sludge load composition prior to using it as an activated carbon feedstock.

3.3.1.2. Effect of temperature and pressure on DM-SA activity.
Short term experiments conducted at different temperatures (120–160 °C) and oxygen partial pressures (2–8 bar) [14] revealed that temperature has a much stronger effect than pressure on the activity of DM-SA. This outcome is in agreement with the reaction order of 0.5–1 commonly reported for CWAO [23]. Hence, in order to execute the CWAO of a 5 g/l phenol solution over DM-SA, the temperature, rather than the oxygen pressure, should be the parameter used to optimise the catalytic activity of the carbon. The DM-SA carbon can provide acceptable activity at 160 °C. However, its long term stability has to be explored at these operating conditions.

3.3.1.3. Stability of DM-SA carbon.
For the CWAO of phenolic compounds over activated carbon, the carbon's mechanical strength and resistance to both burn-off and metal leaching are of great importance for its stability.

Fig. 4 shows the effect, at 160 °C, of raising the oxygen partial pressure from 2 bar to 4 bar on the degree of phenol conversion attained by DM-SA. At 2 bar of partial oxygen pressure, a stable phenol conversion of *ca.* 40% is only observed after *ca.* 40 h of operation, preceded by a short adsorption and a more prolonged activation step. Saturation of the DM-SA carbon is attained in less than 1 h, reflecting its small surface area (Table 2) and adsorption capacity. It has been shown that during this initial period, micropores will predominantly get blocked due to the irreversible adsorption of polymeric molecules formed by oxidative coupling reactions of phenol [24–26]. A possible explanation for the subsequent gradual increase over time of phenol conversion may be that CWAO itself can enhance the active surface area by forming new oxygenated surface groups, which can promote the oxidation of phenol [25,26].

For 4 bar of oxygen partial pressure, a stable level of phenol conversion seems to establish after 20 h at 60%, but after 50 h of
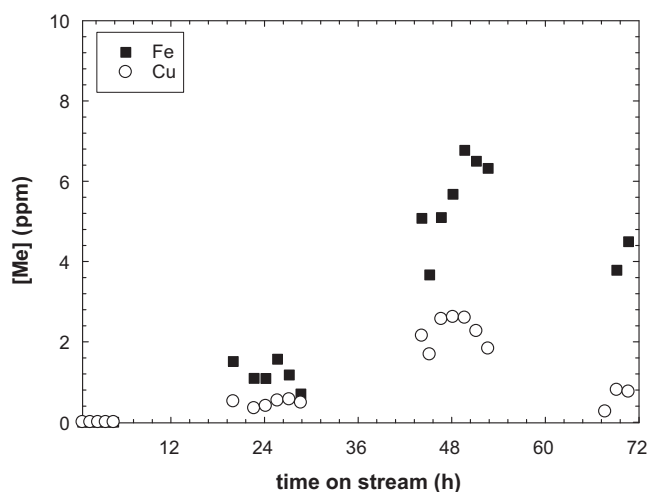

Fig. 5. Release of iron and copper ions during CWAO of phenol over DM-SA: $T = 160\,^\circ C$, $P_{O_2} = 4$ bar, $C_{Ph,0} = 5$ g/l, $\tau_L = 0.12$ h, $F_{air} = 9$ N l/h, $W = 7$ g.

operation the conversion starts to drop, reaching *ca.* 40% at the end of the experiment. Results of weight measurement (ΔW in Table 4) and TGA of the spent CWAO DM-SA carbons [14], suggest that the conversion loss at 4 bar is related to enhanced carbon burn-off (−18.3% at 2 bar against −34% at 4 bar), rather than to deactivation of the DM-SA carbon itself.

Overall, Table 4 indicates that the weight changes incurred by CWAO depends on the oxygen partial pressure as well as the temperature employed, *i.e.* the higher the pressure and temperature, the higher the weight loss. Moreover, previously obtained TGA results [14] indicate that oxidative coupling reactions and irreversible adsorption of polymeric products prevailed over AC burn-off at 120 °C (positive or small negative ΔW and high $-\Delta W_{TGA}$). At 160 °C, however, carbon burn-off is now the dominant phenomenon, (large $-\Delta W$ and small $-\Delta W_{TGA}$) resulting in the aforementioned gradual decline of activity at 160 °C (see Fig. 4).

As discussed in Section 3.1, DM-SA is characterised by a high ash (inorganic) content, comprised of a variety of metals. Inevitably, under the hot and acidic conditions of CWAO, leaching of metals will occur, generating unwanted secondary pollution of the treated effluent. From the start of each CWAO experiment, calcium and magnesium were detected in the liquid effluent at concentrations ranging from 10 to 30 mg/l. Several metals that can have a catalytic effect in CWAO such as zinc, manganese and nickel were detected only at trace levels (<1 mg/l: close to the detection limits). However, significant concentrations were detected of both iron and copper; Fig. 5 illustrates the release of the latter metals during CWAO of phenol at 160 °C and 4 bar of oxygen partial pressure. Fe and Cu are first detected in the liquid effluent after a period of *ca.* 15 h, reaching maximum concentrations of 8 and 3 mg/l, respectively. Overall, the considerable leaching of metal ions corroborates the conclusion that the high weight loss observed at 160 °C stems from the partial disintegration of the carbon structure.

An enhanced understanding of the behaviour of DM-SA carbon at 160 °C was obtained by conducting control experiments with and without phenol using an HPLC analysis time of 35 min. During the experiments without phenol, using nitrogen or air at a partial pressure of 4 bar, 10 and 20 trace area peaks respectively appeared in HPLC analysis of the withdrawn liquid samples. This suggests that the DM-SA carbon releases adsorbed organic material. It may also be the case that the attack of the carbon surface by dissolved oxygen forms organic reaction products and/or aids their dissolution. It is noteworthy that although very small in area, several of the

Table 4
Performance of sludge based and commercial carbons after 72 h of CWAO.

Experiment		DM-SA			DR-SA-PV			DR-SA-LS			AP4-X		
T	P_{O_2}	X_{Ph}	ΔW (%)	Fe[a]	X_{Ph}	ΔW (%)	Fe[a]	X_{Ph}	ΔW (%)	Fe[a]	X_{Ph}	ΔW (%)	Fe[a]
140 °C – 4 bar		0.24	−8.9	–	0.33	−12.1	11	0.19	17.1	9	0.48	22.8	13
160 °C – 2 bar		0.48	−18.3	–	–	–	–	0.18	1.3	1.5	–	–	–
160 °C – 4 bar		0.44	−34.1	8	0.18	−35.5	3	0.43	−33.4	2.5	0.8	−36	25

[a] Maximum concentration of leached Fe in mg/l.

peaks could be clearly assigned to oxalic acid, formic acid, maleic acid hydroquinone, p-benzoquinone and even phenol. The number of peaks then increases drastically for CWAO of phenol, reaching up to 40 or 60 peaks depending on the detection wavelength used for analysis.

3.3.2. Catalytic performance of hardened steam activated DR-SA carbon

3.3.2.1. Performance of DR-SA-PV.
The phenol and TOC removal obtained in two 72 h runs conducted at 4 bar of oxygen partial pressure and at temperatures of 140 °C and 160 °C respectively, are shown in Fig. 6.

DR-SA-PV exhibited a significantly higher activity than DM-SA, but a lower stability, in particular at 160 °C. At 140 °C, the DR-SA-PV carbon underwent a marked activation after initial adsorption, with a rise in phenol conversion from 22 to 47% after 30 h of TOS. Under the same operating conditions, the DM-SA sample exhibited a steady state phenol conversion of 24%. However, during the final 10 to 15 h of the experiment, the DR-SA-PV sample's phenol removal declined from 47% to 33%. Similar trends can be observed in Fig. 6 for the evolution of TOC removal. The loss of activity could be related to burn-off of the DR-SA-PV carbon itself, which is corroborated by weight measurements of the fresh and spent carbon ($\Delta W = −12.1\%$ in Table 4). The carbon oxidation is also accompanied by the dissolution of metal ions into the hot and acidic CWAO effluent. Calcium and magnesium as well as catalytically active metals such as iron and copper, were found to be the main metals leached. Initially, iron and copper release is nil, but after 20 h of operation their concentrations had risen to their maximum values of 10 and 2.5 mg/l, respectively.

The second experiment at 160 °C evidences more clearly the low stability of the DR-SA-PV carbon (see Fig. 6). During the first 24 h of operation, the carbon exhibited a very promising phenol and TOC conversion of ca. 80% and 60% respectively. Then, a steep decrease in catalyst activity occurred, leading to phenol and TOC conversions as low as, respectively, 18% and 10% after 72 h of CWAO. Both metal leaching and carbon burn-off (−35.5%) are enhanced at 160 °C, but these outcomes cannot solely explain the dramatic deactivation observed. Rather, the destruction of the PVA binder material itself is believed to be the primary cause of the observed deactivation. PVA is an organic material and is liable to be degraded by oxidative degradation processes during CWAO, thereby causing the physical disintegration of the DR-SA-PV. Strong experimental evidence for this assumption was found after drying and recovering the spent carbon. The catalyst particles had formed agglomerates and the whole carbon bed was taken out as a compact block. The use of the PVA binder for hardening of the DR-SA is thus not a feasible option and more suitable binder materials that can resist the attack of the hot and acidic CWAO environment must be used.

Fig. 6. Phenol (a) and TOC (b) conversion with time on stream for DR-SA-PV and AP4-X: $C_{Ph,0} = 5$ g/l, $\tau_L = 0.12$ h, $F_{air} = 9$ N l/h, $W = 7$ g.

3.3.2.2. Performance of DR-SA-LS hardened with LSA binder.
The phenol and TOC removal obtained with the LSA hardened, DR-SA-LS carbon are plotted in Fig. 7 for three different operating conditions. In general, the conversion profiles reveal that DR-SA-LS carbon is more stable than the DR-SA-PV carbon, but its activity also exhibits a greater sensitivity to the operating conditions. The two experiments at 140 °C and 4 bar of O_2 and 160 °C and 2 bar of O_2 yielded very similar levels of phenol and TOC removal, but raising the pressure to 4 bar at 160 °C resulted in a 43% improvement in performance. At 160 °C and 4 bar of O_2 the initial phenol conversion after 12 h amounted to 72% for DR-SA-LS, against 78% for DR-SA-PV (see Fig. 6) and 44% for DM-SA (see Fig. 4). As shown in Fig. 7, DR-SA-LS then underwent a decline in activity, but after 72 h of operation it still exhibited phenol and TOC conversions of, respectively, 42% and 32%, with the data indicating that the deterioration in performance had stabilised.

Comparing DR-SA-LS with DM-SA, for the first 24 h DR-SA-LS attained a phenol conversion performance 20–64% higher than DM-SA's. From 36 h onwards, the strongest performance was predominantly exhibited by DM-SA. However, this is likely to arise from its greater leaching of metals: in particular Fe, as is shown in Table 4.

To conclude, the LSA binder is sufficiently stable to withstand the CWAO conditions and moreover, the use of DR-SA-LS can lead to final activities that are considerably higher than those of DR-SA-PV.
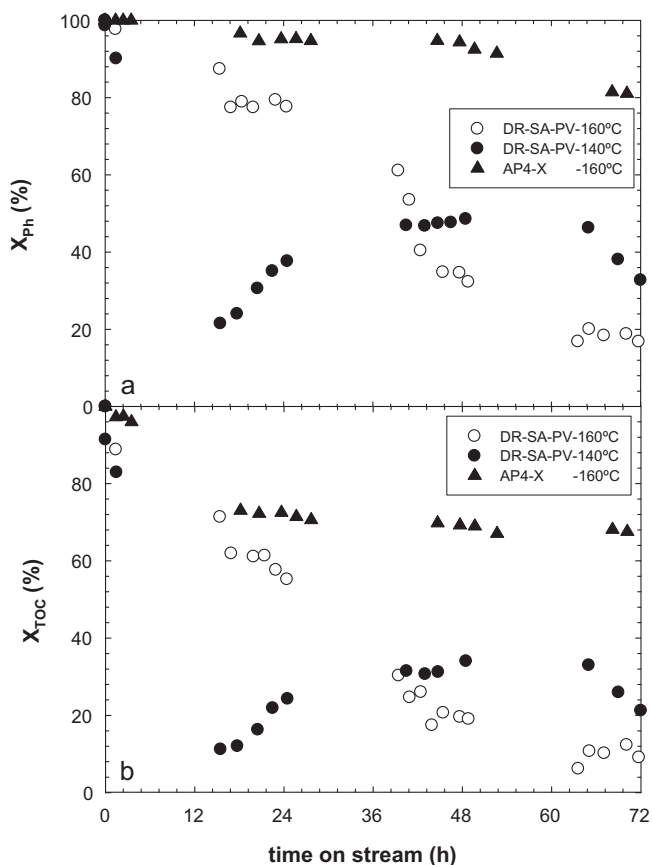
Fig. 7. Phenol (a) and TOC (b) conversion with time on stream for DR-SA-LS and AP4-X: $C_{Ph,0} = 5$ g/l, $\tau_L = 0.12$ h, $F_{air} = 9$ N l/h, $W = 7$ g.
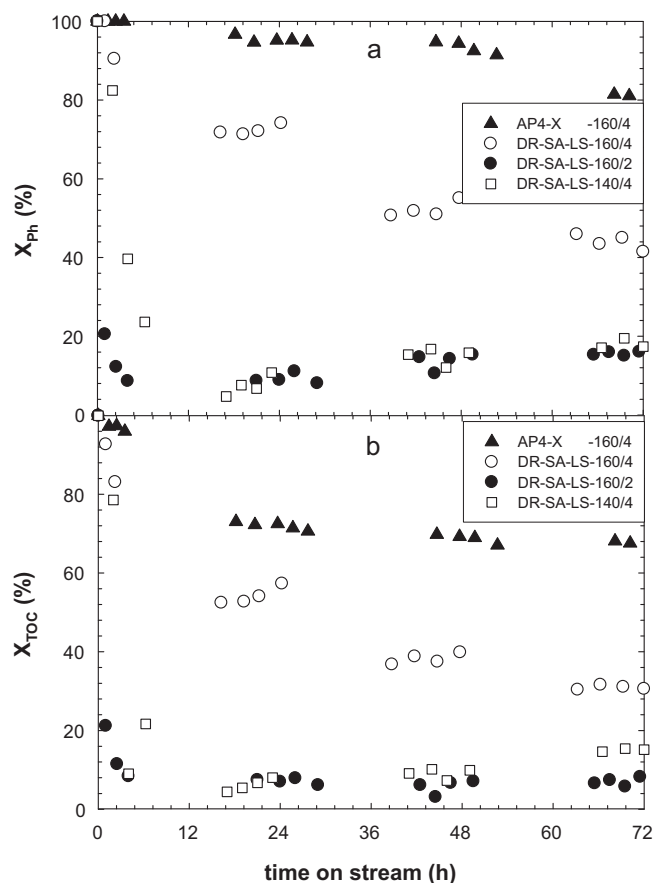
3.3.3. Comparison of commercial carbon AP4-X with SBACs

As shown in Table 4, which lists the phenol conversion values attained at the end of the 72 h experiments, AP4-X outperformed all of the SBACs. At 140 °C, DR-SA-PV attains a percentage conversion value of phenol (X_{Ph}) that is *ca.* 65% of AP4-X's value. However, DR-SA-PV's relatively strong level of performance can, as described in Section 3.3.1, be ascribed to the increased leaching of catalytically active metals arising from its physical disintegration. At the same temperature (140 °C) DM-SA and DR-SA-LS attained X_{Ph} values that were 50% and 40% respectively of the X_{Ph} value attained by AP4-X. At 160 °C, the relative performance of DM-SA and DR-SA-LS improved, attaining 55% and 54% respectively of AP4-X's X_{Ph} value.

The SBACs utilised here all exhibited significant concentrations of catalytically active metals and especially, Fe (see Table 2). Hence, their weaker performance can be largely attributed to their substantially lower surface areas, which are shown in Table 2. However, previous research by this research group [10] has established that the performance of SBACs can be enhanced by the application of HCl washing (this serves to lower the SBACs' ash content, thus increasing their surface area). The utilisation of HCl washed forms of either DM-SA or DR-SA-LS is therefore advised.

It is important to note that, as is displayed in Table 4, AP4-X exhibited the highest weight loss at 160 °C and 4 bar of partial pressure. However, AP4-X has a much lower ash content (11 wt.%), therefore it can sustain a higher degree of carbon burn-off before it exhibits a significant drop in activity. AP4-X also exhibited the highest Fe leaching levels; Fig. 8 shows that for over 48 h of the 72 h experiment, the Fe leaching level displayed by AP4-X was far in excess of DR-SA-LS's.
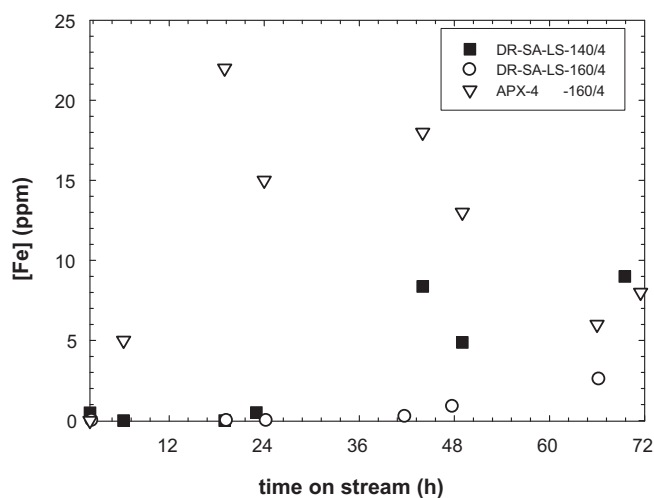

Fig. 8. Release of iron ions for DM-SA-H2 and AP4-X during CWAO of phenol: $C_{Ph,0} = 5$ g/l, $\tau_L = 0.12$ h, $F_{air} = 9$ N l/h, $W = 7$ g.

3.4. Oxidation of phenolic compounds in trickle-bed reactor

In light of its high stability, the DR-SA-LS carbon was used to investigate the oxidation of phenolic compounds in the trickle-bed reactor. In order to avoid exposure of the reactor to potentially corrosive chloride ions, o-chlorophenol was excluded from the tests. Hence, Fig. 9 only displays the compound evolution (X_{Ph}) and TOC conversion obtained for phenol, o-cresol and p-nitrophenol.
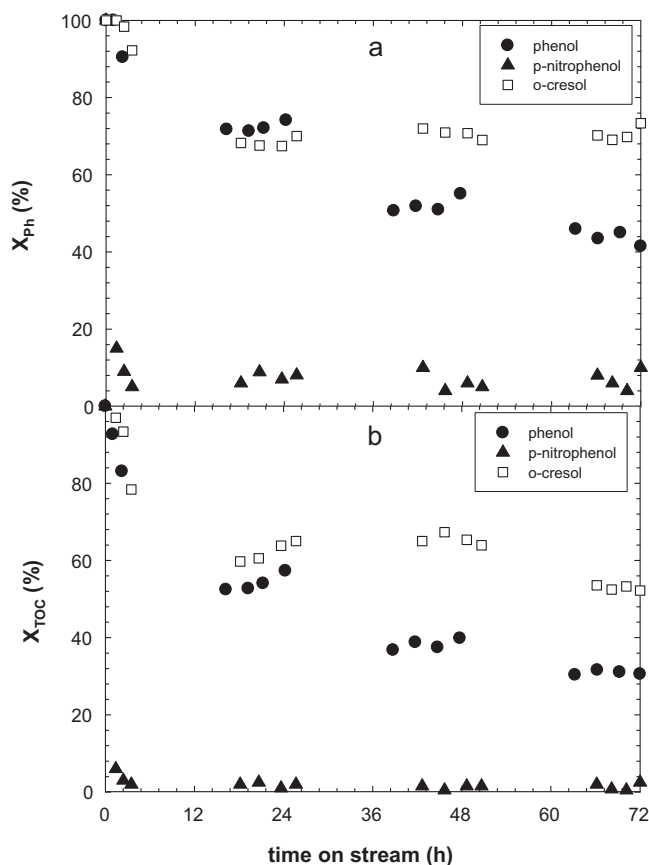

Fig. 9. Phenolic compound (a) and TOC (b) conversion with time on stream for DR-SA-LS carbon: $P = 25$ bar, $T = 160$ °C, $C_0 = 5$ g/l, $\tau_L = 0.12$ h, $F_{air} = 9$ N l/h, $W = 7$ g.

As for the batch oxidation tests, the same order of reactivity established: o-cresol and phenol are readily oxidised in the presence of DR-SA-LS, and p-nitrophenol is found to be resistant to CWAO (conversion < 8%). The best performance is observed in the case of o-cresol oxidation, exhibiting a high and stable compound conversion (*ca.* 70%) over 72 h. A similar initial conversion was verified for phenol, but after 30 h of operation the DR-SA-LS carbon underwent a deactivation process (see Fig. 7), leading to a final conversion of *ca.* 40%. In summary, the degree of CO_2 formation with respect to compound conversion was as high as 75–80% for both phenol and o-cresol. These are promising results because these mineralisation levels are close to the commercial carbon's (80–85%), indicating that the DR-SA-LS is a powerful catalyst for the destruction of certain phenolic compounds.

4. Conclusion

For the batch reactor experiments, two SBACs were tested: DR-SA-C950, which was prepared by steam activation and posterior carbonisation; DM-K-W, which was prepared by chemical (K_2CO_3) activation. Both of the SBACs and the reference commercial carbon (AP4-X) all achieved high TOC removal in the CWAO of phenol, o-cresol and o-chlorophenol, while p-nitrophenol was refractory to CWAO. AP4-X, which had the highest surface area (*ca.* 1000 m^2/g), yielded the highest TOC removal for phenol, but the two SBACs are clearly competitive catalysts for the oxidation of phenolic compounds. DR-SA-C950 is of particular interest as despite its low surface area (269 m^2/g), it achieved the best final TOC removal (87%) in the oxidation of o-cresol. It is noteworthy that during the oxidation of o-chlorophenol, corrosion became a critical issue due to the release of free chloride ions. Hence, treating chlorinated aromatic compounds by CWAO requires the use of reactor materials able to withstand the corrosive conditions that develop.

In the trickle-bed reactor, three steam activated SBACs were investigated. One SBAC was produced from the DMAD sludge (DM-SA). The other two SBACs, which were produced from the DRAW sludge, differed in terms of the techniques and binders utilised to improve their attrition resistance.

Two operating temperatures and different oxygen partial pressures were employed: 140 °C and 160 °C plus 2 and 4 bar, respectively. At 140 °C the SBAC prepared with the PVA binder (DR-SA-PV) exhibited the strongest initial performance. However, this SBAC also exhibited the greatest weight loss and physical deterioration. The high leaching of catalytically active metals induced by its disintegration is believed to have contributed to its strong performance. Thus, the use of the PVA as a binder is not recommended in the manufacture of WAO catalysts.

The most stable SBAC was produced from the DRAW sludge using a lignosulphonate binder (DR-SA-LS). This SBAC exhibited a similar level of performance in the CWAO process to DM-SA. Due to its greater stability, its use is advocated over DM-SA, especially at 160 °C. DR-SA-LS exhibited a substantially lower level of performance than the commercial carbon, but this was due to its significantly higher ash content, which can be reduced through the application of an appropriate ash-dissolution technique such as HCl washing. This group's previous study demonstrated that the reduction in the active metal content (especially Fe) induced by HCl washing was not sufficient to spoil the SBACs' activity [10]. Moreover, in this study it was observed that DR-SA-LS exhibited a lower level of Fe leaching than the commercial carbon.

A key observation made was that the temperature, rather than the oxygen pressure, should be the parameter used to optimise the catalytic activity of the carbon. However, although the use of an operating temperature of 160 °C enhanced the performance of all of the carbonaceous catalysts, it also resulted in a high degree of burn-off of the carbon. Indeed, the highest weight loss was exhibited by the commercial carbon. On the other hand, this outcome highlights the advantage of using carbonaceous catalysts which are low cost and sustainable, *i.e.* are readily replaceable.

Acknowledgements

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